Journal of Thermal Analysis, Vol. 35 (1989) 873–884

PREPARATION, CHARACTERISATION, INFRARED AND THERMAL PROPERTIES OF SOME ADDUCTS OF BIS(8-HYDROXYQUINOLINATO)DIOXOURANIUM(VI)

S. Z. Haider, K. M. A. Malik, M. S. Khan, A. Rahman and *T. Wadsten**

DEPARTMENT OF CHEMISTRY, DHAKA UNIVERSITY,
DHAKA-2, BANGLADESH
*DEVELOPMENT & RESEARCH WAB SURBRUNNSGATAN 58
S–11327 STOCKHOLM, SWEDEN

(Received March 22, 1988)

Several adducts of the coordinatively unsaturated species $UO_2(C_9H_6NO)_2$ with 8-hydroxyquinoline, urea, aniline, methanol, 1,10-phenanthroline, pyridine and water were prepared and characterized. The infrared spectra of these compounds have been recorded and their particular thermal decomposition properties studied. Nitrogen donor ligands have been found to form adducts with $UO_2(C_9H_6NO)_2$ which are thermally more stable than those formed by oxygen donor ligands.

The nature of bonding of the extra molecule of 8-hydroxyquinoline in $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ has inspired several investigations [1–7], but the results are quite contradictory. Crystallographic studies [8] of the chloroform solvate indicated that the extra molecule is directly bound to the metal through the phenolate oxygen. This was also supported by spectral studies [9].

The above tris-complex when heated to 230°, gives the coordinatively unsaturated bis-compound $UO_2(C_9H_6NO)_2$ which is capable of forming adducts with many Lewis bases other than 8-hydroxyquinoline. Comparative studies of such adducts with the 8-hydroxyquinoline adduct should provide further information about the nature of the extra ligand. Study in this field is also scantly, except a noteworthy work by Doretti et al. [10].

In the present paper we report the preparation and characterisation of a number of adducts of $UO_2(C_9H_6NO)_2$ with molecules such as water, methanol, urea, aniline, pyridine and 1,10-phenanthroline. The infra-red absorption bands are listed and the particular thermal properties of these compounds are described and discussed.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

Experimental

Materials and methods

Chemicals, reagents and solvents used in all synthetic and analytical work were analar grade E. Merck and BDH product. Microanalytical data for C, H and N were obtained using a Perkin–Elmer 240 microanalyser. Infra-red spectra (nujol mull) were obtained in the region 200–4000 cm^{-1} using a Perkin–Elmer IR spectrophotometer 2803 and CsBr discs. Differential scanning calorimetric (DSC) measurements were made on a Perkin–Elmer DSC-2 instrument equipped with a Thermal Analysis Data Station (TADS). The thermogravimetric (TG) analysis and registration of the first derivative of the weight loss (DTG) were done simultaneously using a Perkin–Elmer TG-2 instrument under a dynamic gas flow of air or argon of 50 ml/min. The sample sizes were 2–4 mg and the heating rate was 10 deg/min in all experiments.

Preparation

The adducts described in this work were prepared by adopting published procedures [10] with some modification. The bis-chelate, $UO_2(C_9H_6NO)_2$, used as starting material in several preparations, was obtained [5] by heating $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ in a muffle furnace for 2 hours at 270–280° until the red complex turned into a black powder which was then cooled in a desiccator over silica gel.

1. Bis(8-hydroxyquinolinato)(8-hydroxyquinoline)-dioxouranium(VI), $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$.

The complex was prepared by precipitating it from a solution of uranyl nitrate in buffered acetate medium by a 4% solution of 8-hydroxyquinoline in dil. acetic acid [11]. After usual filtration and washing it was oven dried at 110–112° to a constant weight.
Anal. found (%): C 45.74, H 2.74, N 5.95.
Calc. (%): C 46.10, H 2.72, N 5.97.

2. Bis(8-hydroxyquinolinato)(urea)dioxouranium(VI) monohydrate, $UO_2(C_9H_6NO)_2 \cdot CON_2H_4 \cdot H_2O$.

1.0 g urea was added to 1.1 g $UO_2(C_9H_6NO)_2$suspended in 40 ml acetone. The misture was stirred for 1 hour when the colour turned brown. The suspension was left to stand overnight and then filtered. The precipitate was washed with methanol to remove excess urea and then dried in a desiccator over P_2O_5.
Anal. found (%): C 36.93, H 2.73, N 9.06.
Calc. (%): C 35.86, H 2.85, N 8.80.

3. Bis(8-hydroxyquinolinato)(pyridine)dioxouranium(VI) Monohydrate, $UO_2(C_9H_6NO)_2 \cdot C_5H_5N \cdot H_2O$

1.0 g $UO_2(C_9H_6NO)_2$ was dissolved in 60 ml warm pyridine with constant stirring for 30 minutes. The solution was cooled and filtered. The filtrate was then treated with 10 times its volume of *n*-hexane. The dark brown precipitate that formed was collected and dried in a vacuum desiccator over fused calcium chloride.
Anal. found (%): C 40.79, H 2.89, N 6.28.
Calc. (%) for $UO_2(C_9H_6NO)_2 \cdot C_5H_5N \cdot H_2O$: C 42.15, H 2.92, N 6.41.

4. Bis(8-hydroxyquinolinato)(aniline)dioxouranium(VI), $2UO_2(C_9H_6NO)_2 \cdot (C_6H_5NH_2)_2$.

1.2 g $UO_2(C_9H_6NO)_2$ was dissolved in 40 ml warm aniline with constant stirring for 30 minutes. The solution was cooled and filtered. Excess aniline was then removed by repeated extraction with *n*-pentane. The deep brown powder thus obtained was dried in a vacuum desiccator over P_2O_5.
Anal. found (%): C 44.13, H 3.18, N 6.65.
Calc. (%): C 44.25, H 2.94, N 6.45.

5. Bis(8-hydroxyquinolinato)(methanol)dioxouranium(VI) monohydrate, $UO_2(C_9H_6NO)_2 \cdot CH_3OH \cdot H_2O$.

1.1 g $UO_2(NO_3)_2 \cdot 6H_2O$ and 0.8 g $Na(C_9H_6NO)$ were each dissolved in 40 ml methanol and the two solutions mixed. The resulting solution was left overnight when a dark red precipitate collected at the bottom. The precipitate was filtered, washed with methanol and dried in a vacuum desiccator over P_2O_3.
Anal. found (%): C 37.18, H 2.57, N 4.81.
Calc. (%): C 37.5, H 2.47, N 4.61.

6. Bis(8-hydroxyquinolinato)(1,10-phenanthroline)dioxouranium(VI), $UO_2(C_9H_6NO)_2 \cdot C_{12}H_8N_2$.

1.0 g $UO_2(C_9H_6NO)_2 \cdot (CH_3OH)(H_2O)$ was dissolved in 150 ml acetone and excess 1,10-phenanthroline was added to it with constant stirring. The dark orange microcrystalline precipitate that formed was filtered, washed with acetone and dried in a vacuum desiccator over P_2O_5.
Anal. found (%): C 47.14, H 2.60, N 7.34.
Calc. (%): C 48.79, H 2.73, N 7.59.

7. Bis(8-hydroxyquinolinato)dioxouranium(VI) monohydrate, $UO_2(C_9H_6NO)_2 \cdot H_2O$.

An aqueous solution of 0.67 g $Na(C_9H_6NO)$ was added to a solution of 1.0 g $UO_2(NO_3)_2 \cdot 6H_2O$ in 100 ml water. The dark orange precipitate thus obtained turned deep brown on boiling for 10 minutes. The precipitate was filtered, washed with water, alcohol and ether and then dried in a vacuum desiccator over P_2O_5.
Anal. found (%): C 36.74, H 2.68, N 4.75.
Calc. (%): C 37.51, H 2.45, N 4.86.

Discussion

The thermal decomposition patterns (TG and DTG) of the adducts are shown in Figs 1–7, and the results calculated on the basis of the mass of the residue left on decomposition are summarised in Table 1.

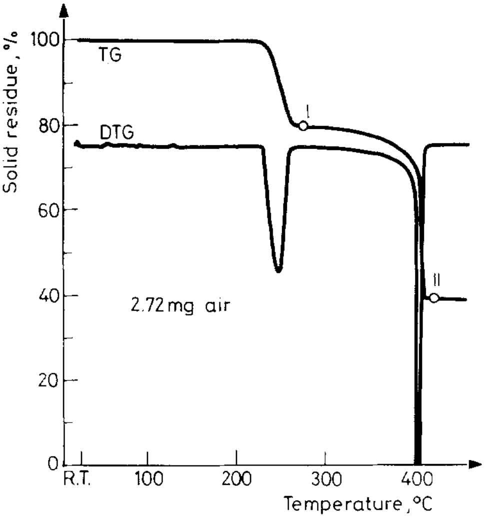

Fig. 1 TG and DTG curves of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$

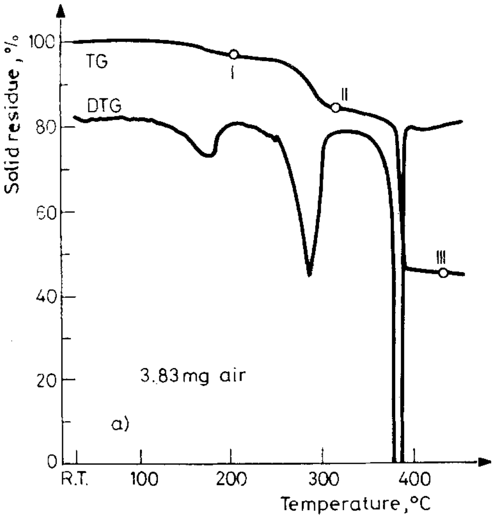

Fig. 2a TG and DTG curves of $UO_2(C_9H_6NO)_2 \cdot CON_2H_4 \cdot H_2O$

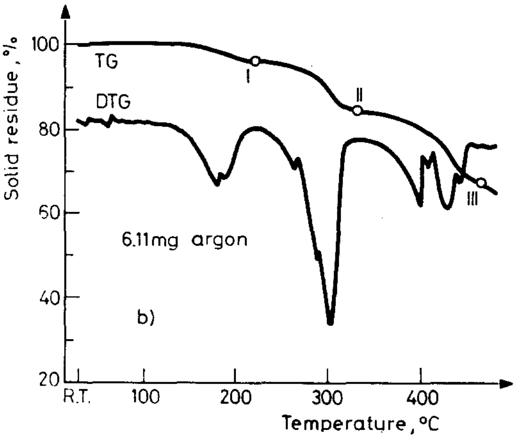

Fig. 2b TG and DTG curves of $UO_2(C_9H_6NO)_2 \cdot CON_2H_4 \cdot H_2O$

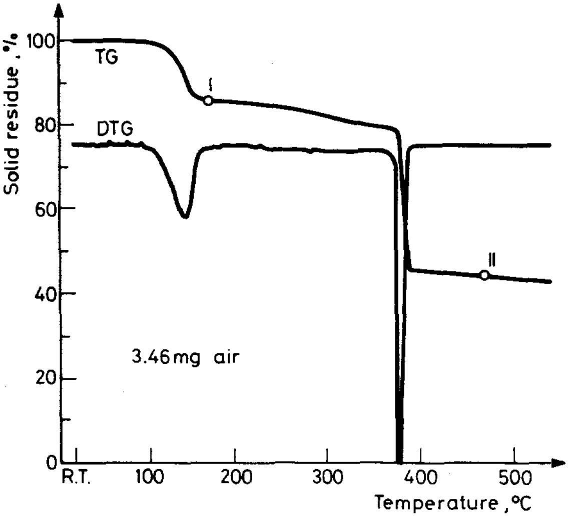

Fig. 3 TG and DTG curves of $UO_2(C_9H_6NO)_2(C_5H_5N \cdot H_2O$

In the case of $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ there is a sudden removal of the adduct C_9H_7NO at 230–250° in a sharp one step endothermic process. The entire bound C_9H_6NO is then lost in an exothermic reaction at 400° giving a residue identified as UO_2 by X-ray powder diffraction. However, in the case of urea adduct which also contain a H_2O molecule, the initial decompositions (upto 320°) in both air and argon atmosphere exhibit similar decomposition steps involving the loss, successively of H_2O and urea giving $UO_2(C_9H_6NO)_2$. The ultimate decomposition product in air is UO_2 but in argon the residue is of indefinite composition.

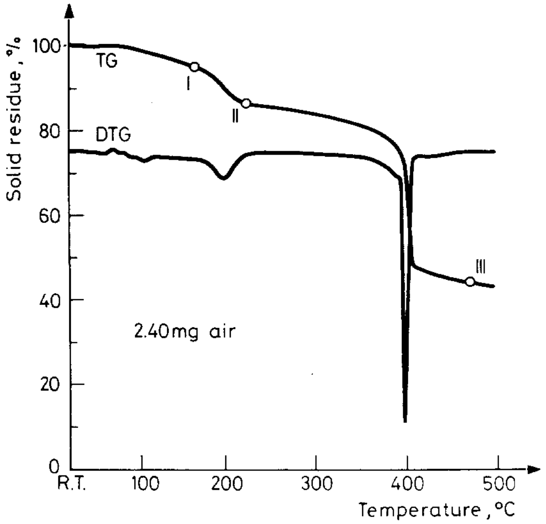

Fig. 4 TG and DTG curves of $2UO_2(C_9H_6NO)_2(C_6H_5NH_2)_2$

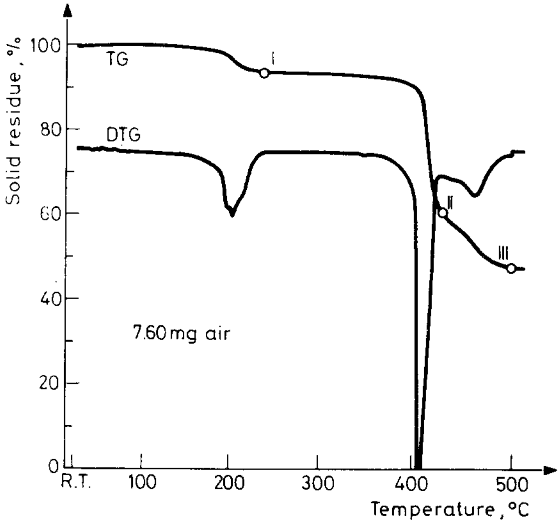

Fig. 5 TG and DTG curves of $UO_2(C_9H_6NO)_2CH_3OH \cdot H_2O$

Formation of U_3O_8 was not supported by experimental results. Thermal decomposition of other adducts can also be explained in similar ways. It should be noted, however, that thermal decomposition of the aniline adduct is best explained on the basis of its formulation as a dimer. In some cases, intermediates which are stable over a range of temperature are formed which subsequently decompose to UO_2 presumably through polymerisation process.

The intermediate formed after the expulsion of the adduct(s) indicated the mode of thermal decomposition in air and argon. In most cases the expulsion of the adduct(s) lead to the formation of $UO_2(OX)_2$ in presence of both air and argon except in the cases of the $C_{12}H_8N_2$ and $CH_3OH \cdot H_2O$ adducts. In these cases indication of polymerisation before the completion of decomposition could be discerned from the thermal diagrams. Expulsion of $CH_3OH \cdot H_2O$ from the

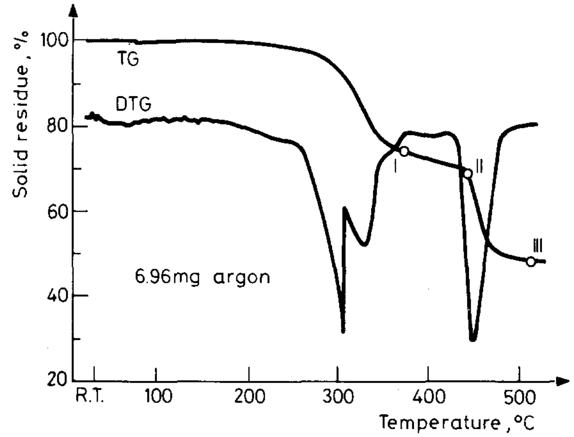

Fig. 6a TG and DTG curves of $UO_2(C_9H_6NO)_2C_{12}H_8N_2$

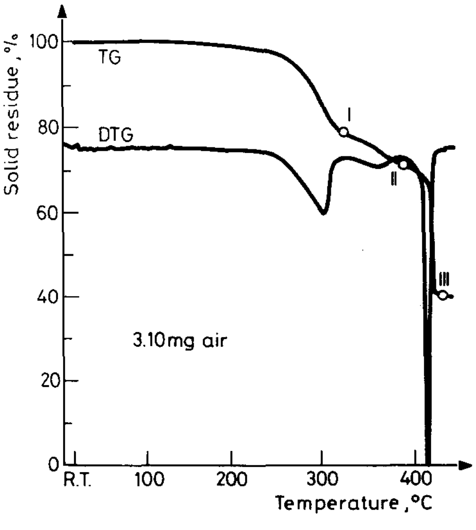

Fig. 6b TG and DTG curves of $UO_2(C_9H_6NO)_2C_{12}H_8N_2$

Table 1 Summary of the results of thermal analysis

Steps	Complex	Temperature, °C	Residue			Remarks
			species	observed, %	calculated %	
1 I	$UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$	230–260 (60 cal/g) (endo)	$UO_2(C_9H_6NO)_2$	79.4	79.4	C_9H_7NO adduct lost in one step.
II	$UO_2(C_9H_6NO)_2$	400 (exo)	UO_2	38.8	38.4	Two ligand units are lost in one sharp step. The residue is UO_2
2 I	$UO_2(C_9H_6NO)_2 \cdot CON_2H_4 \cdot H_2O$ *(air)*	140–210 (30 cal/g) (endo)	$UO_2(C_9H_6NO)_2 \cdot CON_2H_4$	97.0	97.1	Only the H_2O adduct is lost.
II	$UO_2(C_9H_6NO)_2 \cdot CON_2H_4$ *(air)*	260–310 (30 cal/g) (exo)	$UO_2(C_9H_6NO)_2$	85.0	87.7	The urea adduct is lost.
III	$UO_2(C_9H_6NO)_2$ (air)	360–400 (exo)	UO_2	44.0	42.5	Both the ligand units are lost in one sharp step. The residue is UO_2
2 I	$UO_2(C_9H_6NO)_2 \cdot$	160–210 (30 cal/g) (endo)	$UO_2(C_9H_6NO)_2 \cdot CON_2H_4$	96.0	97.1	H_2O is lost
II	$UO_2(C_9H_6NO)_2 \cdot CON_2H_4$ (argon)	260–320 (30 cal/g) (exo)	$UO_2(C_9H_6NO)_2$	84.0	87.7	Urea adduct is lost.
III	$UO_2(C_9H_6NO)_2$ (argon)	400–500 (exo)	Solid residue	65.0	—	Several reactions of complicated nature take place leading to a residue of indefinite compositor

Table 1 (cont.)

Steps	Complex	Temperature, °C	Residue			Remarks
			species	observed, %	calculated, %	
3 I	$UO_2(C_9H_6NO)_2 \cdot C_5H_5N \cdot H_2O$	110–170 (36 cal/g) (endo)	$UO_2(C_9H_6NO)_2$	85.5	85.2	H_2O and C_5H_5N adducts are lost simultaneously.
II	$UO_2(C_9H_6NO)_2$	380 (exo)	UO_2	43.0	41.2	The loss of C_9H_6NO starts around 250 °C, but both the ligands are completely lost in a sharp step at 380 °C giving UO_2 as residue.
4 I+II	$2UO_2(C_9H_6NO)_2 \cdot (C_6H_5NH_2)_2$ (air)	100–215 (23+5 cal/g) (endo)	$2UO_2(C_9H_6NO)_2$	86.0	85.7	Two molecules of adduct are lost from a dimer in two steps.
III	$2UO_2(C_9H_6NO)_2$	390–420 (exo)	$2UO_2$	43.0	41.4	The residue is UO_2.
5 I	$UO_2(C_9H_6NO)_2 \cdot CH_3OH \cdot H_2O$ (air)	120–220 (exo)	$UO_2(C_9H_6NO)_2$	93.5	91.8	CH_3OH & H_2O are lost simultaneously.
II	$4UO_2(C_9H_6NO)_2$	390–420 (exo)	$U_4O_{11}(C_9H_6NO)_2$	61.0	60.0	6 C_9H_6NO units are lost from a tetramer to produce oxygenated intermediate.
III	$U_4O_{11}(C_9H_6NO)_2$	420–490 (exo)	UO_2	47.0	44.4	The residue is UO_2.

Table 1 (cont.)

Steps	Complex	Temperature, °C	Residue			Remarks
			species	observed, %	calculated %	
6 I	$UO_2(C_9H_6NO)_2\cdot C_{12}H_8N_2$ (air)	100–330 (6 cal/g) (exo)	$UO_2(C_9H_6NO)_2$	76.0	75.6	The loss of the adduct molecule begins at a low temperature but the process is completed at a higher temperature.
II	$6\,UO_2(C_9H_6NO)_2$	400 (exo)	$U_6O_{13}(C_9H_6NO)_{10}$	71.0	73.0	Unstable oxygenated intermediate.
III	$U_6O_{13}(C_9H_6NO)_8$	450	$6UO_2$	39.8	39.0	The residue is UO_2.
6 I	$UO_2(C_9H_6NO)_2\cdot C_{12}H_8NO_2$ (argon)	150–350	$UO_2(C_9H_6NO)_2$	76.0	74.0	Adduct lost in two reactions.
II	$6UO_2(C_9H_6NO)_2$	400	$U_6O_{13}(C_9H_6NO)_{10}$	71.0	73.0	Unstable oxygenated intermediate.
III	$U_6O_{13}(C_9H_6NO)_2$	500	Residue	49.0	—	Residue of unknown composition.
7 I	$UO_2(C_9H_6NO)_2\cdot H_2O$	50–120 (8 cal/g) (endo)	$UO_2(C_9H_6NO)_2$	97.0	96.9	The sample probably contains more than one H_2O molecule which is very loosely bound, as indicated by the continuous dehydration starting at nearly room temperature.
II	$UO_2(C_9H_6NO)_2$	400 (exo)	UO_2	48.0	46.9	The loss of C_9H_6NO occurs over a wide range of temperature (200–415 °C) with maximum reaction at 400 °C. the residue is UO_2.

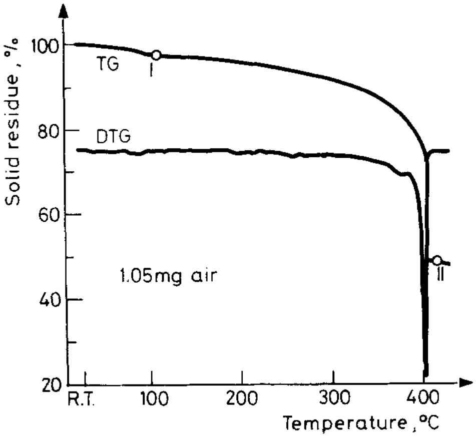

Fig. 7 TG and DTG curves of $UO_2(C_9H_6NO)_2H_2O$

Table 2 Temperatures of maximum reaction for the loss of adduct(s) in air atmosphere

Adduct(s)	Temperature, °C	Energy, cal/g
$C_{12}H_8N_2$	300	6 (exo)
C_9H_7NO	250	60 (endo)
CH_3OH, H_2O	200 (H_2O & CH_3OH)	(exo)
CON_2H_4, H_2O	185 (H_2O)	30 (endo)
	295 (CON_2H_4)	30 (exo)
C_5H_5N, H_2O	145 (H_2O & C_5H_5N)	36 (endo)
$C_6H_5NH_2$	110, 195	28 (endo)
H_2O	110	8 (endo)

particular adduct leads to the formation of the intermediate $U_4O_{11}(OX)_2$, while the phenanthroline adduct after the loss of $C_{12}H_8N_2$ gives the intermediate $U_6O_{13}(OX)_{10}$ in presence of both air and argon. Subsequent decompositions of these oxygenated intermediates in air atmosphere give UO_2 but in argon the end product is of indefinite composition.

The temperature ranges for the expulsion of the adduct molecule(s) from the seven compounds studied are listed in Table 1, whilst the corresponding temperature for maximum reaction in air atmosphere are given in Table 2. It is observed that different adduct molecules are lost at varying temperatures suggesting different binding forces. Considering the temperature for maximum reaction as an indication of the thermal stability of a given complex, it may be suggested that the water and the phenanthroline adducts are, respectively, the least and the most thermally stable compounds described in this work.

There are many similarities in the properties observed between these materials and the corresponding thorium-complexes recently published in this journal [12].

* * *

We thank the University Grants Commission (BD) for a junior fellowship to AR and the Swedish Institute for a visiting grant to SZH.

References

1 F. J. Frare, J. Amer. chem. Soc., 35 (1933) 4362.
2 T. Moeller and M. V. Ramaniah, J. Amer. Chem. soc., 75 (1953) 3946.
3 E. P. Bullwinkel and P. Nobel, J. Amer. Chem. Soc., 80 (1958) 2955.
4 T. H. Von Tassel, W. W. Wendlendt and E. Strum, J. Amer. Chem. Soc., 83 (1961) 810.
5 A. Corsini and J. Abraham, Talanta, 15 (1968) 562.
6 R. G. Charles, H. Fraiser, R. Friedel, L. E. Hillerd and W. D. Johnston, Spectrochim. Acta, 8 (1956) 1.
7 J. E. Fleming and H. Lynton, Can. J. Chem., 45 (1967) 1637.
8 D. Hull, A. D. Rae and T. N. Waters, Acta Cryst., 22 (1967) 258.
9 A. Corsini, J. Abraham and M. J. Thomson, Talanta, 18(5) (1971) 481; J. C. S. Chem. Comm., 21 (1967) 1101.
10 L. Doretti, S. Faleschini, S. Sitran and G. Faraglia, J. Coord. Chem., 6 (1963) 115.
11 T. Moeller and D. H. Wilkins, "Inorganic Synthesis", McGraw-Hill, New York, Vol. 4, 1953, p. 101.
12 S. Z. Haider, K. M. Malik, A. Rahman and T. Wadsten, J. Thermal Anal., 31 (1986) 621.

Zusammenfassung — Es wurden einige Addukte des koordinativ ungesättigten $UO_2(C_9H_6NO)_2$ mit 8-Hydroxyquinolin, Harnstoff, Anilin, Methanol, 1,10-Phenanthrolin, Pyridin und Wasser hergestellt und charakterisiert. Es wurden die IR-Spektren der Verbindungen aufgenommen sowie deren einzelne thermische Zersetzungseigenschaften untersucht. Liganden mit Stickstoffdonor formen mit $UO_2(C_9H_6NO)_2$ thermisch stabilere Addukte als Liganden mit Sauerstoffdonor.

Резюме — Получены и охарактеризованы несколько аддуктов координационно ненасыщенного $UO_2(C_9H_6NO)_2$ с 8-оксихинолином, мочевиной, анилином, метанолом, 1,10-фенантролином, пиридином и водой. Изучены ИК спектры этих соединений и их специфическое термическое разложение. Установлено, что азотсодержащие лиганды образуют с $UO_2(C_9H_6NO)_2$ термически более устойчивые аддукты, чем кислородсодержащие лиганды.